

Melting in large sodium clusters: An orbital-free molecular dynamics study.

Andrés Aguado, José M. López, and Julio A. Alonso

Departamento de Física Teórica, Universidad de Valladolid, Valladolid 47011, Spain

M. J. Stott

Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada

The melting-like transition in sodium clusters Na_N , with $N=55$, 92, and 142 is studied by using constant-energy molecular dynamics simulations. An orbital-free version of the Car-Parrinello technique is used which scales linearly with system size allowing investigation of the thermal behaviour of large clusters. The ground state isomer of Na_{142} (an uncomplete three-shell icosahedron) melts in two steps: the first one (at ≈ 240 K) is characterized by the high mobility of the atoms located on the cluster surface; the second, homogeneous melting (at ≈ 270 K), involves diffusive motion of all the atoms across the cluster. For the case of Na_{92} , the icosahedral structure has a larger number of surface vacancies, and melts in two well separated steps, surface melting at ≈ 130 K and homogeneous melting at ≈ 240 K. Na_{55} , a complete two-shell icosahedron, melts in a single stage at ≈ 190 K. Our results on homogeneous melting for Na_{142} and Na_{92} are in excellent agreement with recent experimental determinations of melting temperatures and latent heats. However, the experimentally observed enhancement of the melting temperature around $N=55$ is not reproduced by the calculations.

PACS numbers: 36.40.Ei 64.70.Dv

I. INTRODUCTION

The melting-like transition in finite clusters consisting of a small number of atoms is of fundamental interest as clusters are often produced in a disordered "liquid" state,¹ and it is also relevant to applications of clusters. For example, the catalytic activity of small platinum clusters depends critically on their melting temperatures.² Recent experimental advances reveal some details of the melting-like transition but, at the same time, show new and interesting features. Martin³ determined the cluster size dependence of the melting temperature T_m of large sodium clusters, composed of thousands of atoms, by observing the vanishing of the atomic shell structure in the mass spectra upon heating. It was concluded that T_m grows with cluster size, but the results did not extrapolate yet to the T_m of the bulk. Peters *et al.*⁴ performed X-ray diffraction experiments on large (50 nm) Pb clusters and observed the occurrence of surface melting before homogeneous melting. Electron diffraction⁵ may also help in detecting a surface melting stage.² Haberland and coworkers⁶ have studied the variation with temperature of the photofragmentation spectra of Na_N ($N=50-200$) clusters, and have deduced the melting temperatures of the clusters. They find that for some cluster sizes the melting temperature is a local maximum not in exact correspondence with either electronic or atomic shell closing numbers, but bracketed by the two, suggesting that both effects are relevant to the melting process.

A number of computer simulations of melting in small metallic and nonmetallic clusters has been reported, the majority of which employed phenomenological interatomic potentials.⁷⁻⁹ The use of such parameterized potentials allows the consideration of long dynamical trajectories for large clusters.^{8,9} *Ab initio* methods,¹⁰ which have also been used, accurately treat the electronic structure of the cluster, but are much more expensive

computationally and are usually restricted to the study of small clusters for short dynamical trajectories.¹¹ Recently, Rytönen *et al.*¹² have performed *ab initio* molecular dynamics (aiMD) simulations of the melting of a sodium cluster with 40 atoms, but such a large cluster required the use of a fast heating rate. These aiMD treatments use the Kohn-Sham (KS) form¹³ of density functional theory (DFT), and orthogonalization of the one-electron KS orbitals is the limiting step in their performance. However, DFT shows that the total energy of the electronic system can be expressed in terms of just the electronic density,¹⁴ and orbital-free (OF) versions of the aiMD technique based on the electron density have been developed and employed, both in solid state^{15,16} and cluster¹⁷⁻²⁰ applications. These OF methods scale linearly with the system size allowing the study of larger clusters for longer simulation times than typical aiMD simulations. However, quantum shell effects are neglected, so that features associated with electronic shell closings are not reproduced.

Previously,²⁰ we have used the orbital-free molecular dynamics (OFMD) method to study the melting process in small sodium clusters, Na_8 and Na_{20} , clusters outside the range covered by Haberland's photofragmentation experiments.⁶ Here, we report constant energy OFMD simulations in a study of the melting-like transition in larger clusters, Na_{55} , Na_{92} and Na_{142} , which are within the size range covered in those experiments, and for which a full *ab initio* treatment of their thermal properties would be impractical. Even for the OFMD method those large clusters represent a very substantial computational effort. The aim of our work is to study the mechanisms by which the melting-like transition proceeds in these large clusters. In the next section we briefly present some technical details of the method. The results are presented and discussed in section III and, finally, section IV summarizes our main conclusions.

II. THEORY

The orbital-free molecular dynamics method is a Car-Parrinello total energy scheme¹⁰ which uses an explicit kinetic-energy functional of the electron density, and has the electron density as the dynamical variable, as opposed to the KS single particle wavefunctions. In contrast to simulations which use empirical interatomic potentials, the detailed electronic structure and the electronic contribution to the energy and the forces on the ions are recalculated efficiently every atomic time-step. The main features of the energy functional and the calculational scheme have been described at length in previous work,^{15,17,19,20} and details of our method are as described by Aguado *et al.*²⁰ In brief, the electronic kinetic energy functional of the electron density, $n(\vec{r})$, corresponds to the gradient expansion around the homogeneous limit through second order^{14,21-23}

$$T_s[n] = T^{TF}[n] + \frac{1}{9}T^W[n], \quad (1)$$

where the first term is the Thomas-Fermi functional

$$T^{TF}[n] = \frac{3}{10}(3\pi^2)^{2/3} \int n(\vec{r})^{5/3} d\vec{r}, \quad (2)$$

and the second is the lowest order gradient correction, where T^W , the von Weizsäcker term, is given by

$$T^W[n] = \frac{1}{8} \int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})} d\vec{r}. \quad (3)$$

The local density approximation is used for exchange and correlation.^{24,25} In the external field acting on the electrons, $V_{ext}(\vec{r}) = \sum_n v(\vec{r} - \vec{R}_n)$, we take v to be the local pseudopotential of Fiolhais *et al.*,²⁶ which reproduces well the properties of bulk sodium and has been shown to have good transferability to sodium clusters.²⁷

The cluster is placed in a unit cell of a cubic superlattice, and the set of plane waves periodic in the superlattice is used as a basis set to expand the valence density. Following Car and Parrinello,¹⁰ the coefficients of that expansion are regarded as generalized coordinates of a set of fictitious classical particles, and the corresponding Lagrange equations of motion for the ions and the electron density distribution are solved as described in Ref. 20.

The calculations for Na₉₂ and Na₁₄₂ used a supercell of edge 71 a.u. and the energy cut-off in the plane wave expansion of the density was 8 Ryd. For Na₅₅, the cell edge was 64 a.u. and the energy cut-off 10 Ryd. In all cases, a 64×64×64 grid was used. Previous tests²⁰ indicate that the cut-offs used give good convergence of bond lengths and binding energies. The fictitious mass associated with the electron density coefficients ranged between 1.0×10^8 and 3.3×10^8 a.u., and the equations of motion were integrated using the Verlet algorithm²⁸ for both electrons and ions with a time step ranging from $\Delta t = 0.73 \times 10^{-15}$ sec. for the simulations performed at the lowest temperatures, to $\Delta t = 0.34 \times 10^{-15}$ sec. for those at the highest ones. These choices resulted in a conservation of the total energy better than 0.1 %.

The first step of the simulations was the determination of low temperature isomers for each of the three cluster sizes. For such large clusters it is very difficult to find the global minimum because the number of different local minima increases exponentially with the number of atoms in the cluster. Instead, one has to adopt structures that are likely to have the main characteristics of the ground state. We have assumed icosahedral growth. Thus, for Na₁₄₂ we removed five atoms from the surface of a 147 atom three-shell perfect icosahedron. For Na₉₂, we constructed an icosahedral isomer by following the growing sequence described by Montejano-Carrizales *et al.*,²⁹ and for Na₅₅ we took a perfect two-shell icosahedron. We have also used dynamical simulated annealing,¹⁰ to generate low temperature isomers, but this procedure always led to amorphous structures for Na₉₂ and Na₁₄₂, and to a nearly icosahedral structure for Na₅₅.

Several molecular dynamics simulation runs at different constant energies were performed in order to obtain the caloric curve for each icosahedral isomer. The initial positions of the atoms for the first run were taken by slightly deforming the equilibrium low temperature geometry of the isomer. The final configuration of each run served as the starting geometry for the next run at a different energy. The initial velocities for every new run were obtained by scaling the final velocities of the preceding run. The total simulation times varied between 8 and 18 ps for each run at constant energy.

A number of indicators to locate the melting-like transition were employed. Namely, the specific heat defined by³⁰

$$C_v = [N - N(1 - \frac{2}{3N-6}) < E_{kin} >_t < E_{kin}^{-1} >_t]^{-1}, \quad (4)$$

where N is the number of atoms and $<>_t$ indicates the average along a trajectory; the diffusion coefficient,

$$D = \frac{1}{6} \frac{d}{dt} < r^2(t) >, \quad (5)$$

which is obtained from the long time behaviour of the mean square displacement $< r^2(t) > = \frac{1}{Nn_t} \sum_{j=1}^{n_t} \sum_{i=1}^N [\vec{R}_i(t_{0_j} + t) - \vec{R}_i(t_{0_j})]^2$, where n_t is the number of time origins, t_{0_j} , considered along a trajectory; the time evolution of the distance between each atom and the center of mass of the cluster

$$r_i(t) = |\vec{R}_i(t) - \vec{R}_{cm}(t)|, \quad (6)$$

and finally, the radial atomic density, averaged over a whole dynamical trajectory,

$$\rho(r) = \frac{dN_{at}(r)/dr}{4\pi r^2}, \quad (7)$$

where $dN_{at}(r)$ is the number of atoms at distances from the center of mass between r and $r + dr$.

III. RESULTS

The lowest energy structure of sodium clusters of medium size is not known. DFT calculations for

Na₅₅ performed by Kümmel *et al.*³¹ using an approximate structural model (CAPS model, where the total pseudopotential of the ionic skeleton is cylindrically averaged)³² give a structure close to icosahedral. Near-threshold photoionization mass spectrometry experiments suggest icosahedral structures for large sodium clusters with more than 1400 atoms,³³ so incomplete icosahedral structures are plausible candidates for Na₉₂ and Na₁₄₂. For this reason we have adopted for Na₁₄₂ an isomer obtained by removing five atoms from a perfect three-shell icosahedron. The icosahedral growing sequence in nickel clusters has been studied by Montejano-Carrizales *et al.*,²⁹ who have shown that the 12 vertices of the outermost shell are the last sites to be occupied. Assuming the same growth sequence for sodium clusters, we have removed five atoms from the vertex positions of Na₁₄₇, testing all possibilities, and have then relaxed the resulting structures. In the most stable structure thus formed, the five vacancies form a pentagon. For Na₉₂, we have adopted the umbrella growing model of Montejano-Carrizales *et al.*²⁹ The resulting structure corresponds to three complete umbrellas capping a Na₅₅ icosahedron. Low-temperature dynamical trajectories verify that these structures are indeed stable isomers of Na₉₂ and Na₁₄₂. The icosahedral isomers are more stable than the lowest energy amorphous isomers which were found by simulated annealing (0.017 eV/atom and 0.020 eV/atom for Na₉₂ and Na₁₄₂ respectively). Calvo and Spiegelmann have studied sodium clusters in the same size range, using pair potential and tight-binding (TB) calculations,⁹ and have also predicted icosahedral structures for Na₅₅, Na₉₃, Na₁₃₉ and Na₁₄₇.

For each icosahedral cluster we have calculated the so-called caloric curve which is the internal temperature as a function of the total energy, where the internal temperature is defined as the average of the ionic kinetic energy³⁰. A thermal phase transition is indicated in the caloric curve by a change of slope, the slope being the specific heat; the height of the step gives an estimate of the latent heat of fusion. However, melting processes are more easily recognised as peaks in the specific heat as a function of temperature. These have been calculated directly from eq. (4) and are shown together with the caloric curves in figures 1–3. The specific heat peaks occur at the same temperatures as the slope changes of the caloric curve giving us confidence in the convergence of our results as the two quantities have been obtained in different ways.

The specific heat curve for Na₁₄₂ (fig. 1) displays two main peaks at $T_s \approx 240$ K and $T_m \approx 270$ K, suggesting a two step melting process, but these are so close that only one slope change in the caloric curve can be distinguished. Our analysis below shows that homogeneous melting occurs at $T_m \approx 270$ K in excellent agreement with the experiments of Haberland and coworkers,⁶ who give an approximate value of 280 K. The latent heat of fusion estimated from the step at T_m in the caloric curve is $q_m \approx 15$ meV/atom, again in good agreement with the experimental value of ~ 14 meV/atom. However, the premelting stage at $T=T_s$ is not detected in the experiments, but our results are not inconsistent with this

because the two calculated peaks in the specific heat are close together and the height of the first peak is much smaller than that of the second; consequently they could be difficult to distinguish experimentally. Calvo and Spiegelmann⁹ have performed Monte Carlo (MC) simulations using a semiempirical many-atom potential, and the lowest-energy isomer they found for Na₁₃₉ was also an incomplete three-shell icosahedron, in this case with 8 surface vacancies. They also report two close peaks in the specific heat curve indicating a two-step melting process, with $T_s \approx 210$ K and $T_m \approx 230$ K. They concluded that these two temperatures become closer as the cluster size increases, so that for clusters with more than about 100 atoms there is effectively just one peak in the specific heat and a single-step melting. Tight binding (TB) molecular dynamics calculations were performed by the same authors.⁹ Although the melting temperatures were found to be different from those obtained with the semiempirical potentials (TB tends to overestimate the experimental values, while empirical potentials tend to underestimate them), the qualitative picture of melting in two close steps was the same.

The results for Na₉₂ are shown in fig. 2. Two-step melting is again observed, with a small prepeak in the specific heat at $T_s \approx 130$ K and a large peak, corresponding to homogeneous melting, at $T_m \approx 240$ K. In this case T_s and T_m are well separated, but the first peak is much smaller than the second, which could again account for the absence of the prepeak in the experiments. The calculated temperature and latent heat for the homogeneous melting stage, $T_m \approx 240$ K and $q_m \approx 8$ meV/atom, are again in excellent agreement with the experimental values,⁶ 250 K and 7 meV/atom respectively. Calvo and Spiegelmann⁹ arrive at similar conclusions based on MC simulations for Na₉₃ using phenomenological potentials: a small bump near 100 K and a main peak near 180 K. Their TB simulations give values for those two temperatures roughly 100 K higher.

The experiments⁶ indicate a substantial enhancement of the melting temperature in the size region around $N=55$ atoms. The reported melting temperature of Na₅₅⁺ is 325 K, surprisingly higher than that of Na₁₄₂⁺, which is a local maximum in the size region of the third icosahedral shell closing. Our simulations do not reproduce this enhancement of T_m for Na₅₅ and predict that this cluster melts in a single stage at $T_m \approx 190$ K (fig. 3), a result found also by Calvo and Spiegelmann.⁹ The OFMD method does not account for electronic quantum-shell effects, and full KS calculations may be needed to clarify this discrepancy, although it is not clear *a priori* how electronic shell effects could shift the value of T_m by such a large amount. Of course, another possibility is that the icosahedron is not the ground state isomer. However, Kümmel *et al.*³¹ have recently found that the experimental photoabsorption spectrum of Na₅₅⁺ is best reproduced with a slightly oblate isomer which is close to icosahedral. We have also investigated a bcc-like growing sequence finding that bcc structures are less stable than icosahedral ones for all cluster sizes studied. Also, we studied the melting behavior of a Na₅₅ isomer with bcc structure and did not find an enhanced melting temperature for it

either. In summary, the discrepancy between experiment and theory for Na₅₅ deserves further attention.

Various quantities have been analyzed in order to investigate the nature of the transitions at T_s and T_m . The short-time averages (sta) of the distances between each atom and the center of mass of the cluster, $\langle r_i(t) \rangle_{sta}$, have been calculated, and the cluster evolution during the trajectories has been followed visually using computer graphics. The $\langle r_i(t) \rangle_{sta}$ curves for Na₁₄₂ are presented in Figs. 4-6 for three representative temperatures. At low temperatures (Fig. 4) the values of $\langle r_i(t) \rangle_{sta}$ are almost independent of time. The movies show that the clusters are solid, the atoms merely vibrating around their equilibrium positions. Curve crossings are due to oscillatory motion and slight structural relaxations rather than diffusive motion. At this low temperature quasidegenerate groups which are characteristic of the symmetry can be distinguished: one line near the centre of mass of the cluster identifies the central atom (its position does not exactly coincide with the center of mass because of the location of the five surface vacancies); 12 lines correspond to the first icosahedral shell; another 42 complete the second shell, within which we can distinguish the 12 vertex atoms from the rest because their distances to the centre of mass are slightly larger; finally, 82 lines describe the external shell, where again we can distinguish the 7 vertex atoms from the rest.

The radial atomic density distributions with respect to the cluster center, $\rho(r)$, are shown for Na₁₄₂ in Fig. 7. At the lowest temperature, $T=30$ K, the atoms in the icosahedral isomer are distributed in three well separated shells, a surface shell and two inner shells; as discussed above, subshells form in the second and third shells. The shell structure is still present at $T=130$ K.

Figures 5 and 7 show that at $T=160$ K the atomic shells of the Na₁₄₂ cluster are still well defined, but the movies reveal isomerization transitions, similar to those found at the beginning of the melting-like transition of Na₈ and Na₂₀,²⁰ with no true diffusion. These isomerizations involve the motion of vacancies in the outer shell, in such a way that different isomers are visited which preserve the icosahedral structure. The onset of this motion is gradual and does not lead to features in the specific heat, although it is detected in the temperature evolution of the diffusion coefficient (see Fig. 8 and discussion below). The true surface melting stage does not develop in the icosahedral isomer until a temperature of $T_s \approx 240$ K is reached.

Fig. 6 shows the time evolution of $\langle r_i \rangle_{sta}$ for Na₁₄₂ at a temperature $T=361$ K at which the cluster is liquid with all the atoms diffusing throughout the cluster. Some specific cases of atoms that at the beginning of the simulation are near (far from) the center of mass of the cluster and end in a position far from (near) the center of mass of the cluster are shown in boldface. The atomic density distribution at 280 K, a temperature just above the melting point, is nearly uniform across the cluster, a radial expansion of the cluster by about 5 bohr units is evident, and the surface is more diffuse.

The $\langle r_i(t) \rangle_{sta}$ curves for Na₉₂ at low temperature are qualitatively similar to those of Na₁₄₂. Na₉₂ shows

surface melting at $T_s \approx 130$ K. This temperature is in the range where the isomerization processes in Na₁₄₂ set in, but the larger number of vacancies in the surface shell of Na₉₂ allows for more rapid surface diffusion and these processes give rise to a distinct peak in the specific heat.

Na₅₅ is a perfect two-shell icosahedron, so surface atoms have no empty sites available to move to, and diffusion within an atomic shell is almost as difficult as diffusion across different shells. When the surface atoms have enough energy to exchange positions with one another they can as easily migrate throughout the whole cluster, and melting proceeds in a single stage at 190 K. Calvo and Spiegelmann⁹ have suggested that this one-step melting is associated with a large energy gap between the ground state icosahedral structure and the closest low-lying isomers, but this cannot be a general result for perfect icosahedral metallic clusters, as the details of melting are material dependent. For example, a surface melting stage has been observed in simulations of icosahedral Ni₅₅.³⁴

The variation of the diffusion coefficient with temperature is shown in Fig. 8 for Na₁₄₂. At temperatures less than about 140K, D is close to zero, indicating only an oscillatory motion of the atoms. For temperatures between 140K and T_s , the diffusion coefficient increases indicating that the atoms in the cluster are not undergoing simple vibrational motion; the atomic motions are, nevertheless, of the special kind discussed above that preserve the icosahedral structure. The slope of $D(T)$ increases appreciably at T_s when surface melting occurs, but there is no noticeable feature when the cluster finally melts at T_m . The features of $D(T)$ for Na₉₂ which are not shown here, are very similar: $D(T)$ is very sensitive to the surface melting stage, where appreciable diffusive motion begins, and the homogeneous melting transition is masked by that effect. We conclude that the $D(T)$ curve is a good indicator of homogeneous melting only in those cases where the surface melting stage is absent, as for example in Na₅₅.

Our results suggest that the melting transition in large icosahedral sodium clusters occurs in a smaller temperature range than for small clusters such as Na₈ or Na₂₀,²⁰ at least near an icosahedral shell closing. Furthermore, the size of any prepeak diminishes with respect to the main homogeneous melting peak as the cluster size increases, that is as the fraction of atoms that can take part in premelting decreases. Consequently, a homogeneous melting temperature can be defined with less ambiguity for large clusters. These comments apply to the caloric and the specific heat curves, which are the quantities amenable to experimental measurement. In contrast, microscopic quantities such as the diffusion coefficient D or the $\langle r_i(t) \rangle_{sta}$ curves are very sensitive to any small reorganization in the atomic arrangement, and it is difficult to determine the melting transition from the variation of these quantities with temperature. A helpful structural, as opposed to thermal, indicator of the melting transition in medium-sized or large clusters is the shape of the radial atomic density distribution. The atomic density displays pronounced shell structure at low temperatures which is smoothed out at interme-

diates temperatures where the vacancy diffusion and/or surface melting mechanisms are present. Above T_m the density is flat.

In figure 9 we compare the calculated values of the melting temperature with the experimental values. Our earlier results for Na_8 and Na_{20} ²⁰ are also included, although for such small sizes there is some ambiguity in defining a melting temperature. There is excellent agreement with the experimental results for Na_{92} and Na_{142} .⁶ Measurements of the temperature dependence of the photoabsorption cross sections for Na_n^+ ($n=4-16$) have recently been reported.^{35,36} Although the spectra do not show evidence of a sharp melting transition, some encouraging comparison between theory and experiment can be made. The experimental spectra do not change appreciably upon increasing the cluster temperature, until at $T=105$ K (the value given as the experimental melting temperature of Na_8 in Fig. 9) the spectra begin to evolve in a continuous way. In our study of the melting behaviour of Na_8 ²⁰ we found a broad transition starting at $T=110$ K and continuing until $T=220$ K, at which point the “liquid” state was fully developed. This may explain the absence of abrupt changes in the experimental photoabsorption spectrum with temperature. In any case, we feel that the good agreement between theory and experiment may extend to the small sizes. However, our method is not expected to give accurate results if oscillations in the melting temperature with cluster size arise as a consequence of electronic shell effects, which is not yet known. The discrepancy for Na_{55} remains intriguing. In this regard it is noteworthy that our calculated melting temperatures for the three large clusters fit precisely the expected large N behaviour, $T_m(\text{Na}_N)=T_m(\text{bulk}) + C/N^{2/3}$, where C is a constant, and yield as a bulk melting temperature $T_m(\text{bulk})=350$ K, which is close to the observed value of 371 K. A similar extrapolation to the bulk melting temperature is not evident in the experimental data.

As it is well known that the specific isomer used to start the heating dynamics can affect the details of the melting transition,³⁷ we have also studied the melting of amorphous Na_{92} and Na_{142} clusters that we obtained by a simulated annealing. For the amorphous Na_{142} cluster bulk melting occurred at the same temperature, $T=270$ K, as for the icosahedral cluster, while surface melting took place at a much lower temperature, $T=130$ K. However, melting of the amorphous Na_{92} cluster took place over a wide temperature, and no sharp transitions were detected. We attach little significance to these results as the initial structures and the melting behaviour must depend on the details of the annealing, and the subsequent heating.

IV. DISCUSSION AND CONCLUSIONS

A few comments regarding the quality of the simulations are perhaps in order here. The orbital-free representation of the atomic interactions, although much more efficient than the more accurate KS treatments, is still substantially more expensive computationally than a simula-

tion using phenomenological many-body potentials. Such potentials contain a number of parameters that are usually chosen by fitting some bulk and/or molecular properties. In contrast our model is free of external parameters, although there are approximations in the kinetic and exchange-correlation functionals. The orbital-free scheme accounts, albeit approximately, for the effects of the detailed electronic distribution on the total energy and the forces on the ions. We feel that this is particularly important in metallic clusters for which a large proportion of atoms are on the surface and experience a very different electronic environment than an atom in the interior. Furthermore, the adjustment of the electronic structure and consequently the energy and forces to rearrangements of the ions is also taken into account. But the price to be paid for the more accurate description of the interactions is a less complete statistical sampling of the phase space. The simulation times are substantially shorter than those that can be achieved in phenomenological simulations. Longer simulations would be needed in order to fully converge the heights of the specific heat peaks, or in order to observe a van der Waals loop in the caloric curves, to mention two examples. But we expect that the locations of the various transitions are reliable. All the indicators we have used, both thermal and structural ones, are in essential agreement on the temperature at which the transitions start. As we discussed in a previous paper,²⁰ longer trajectories may induce just a slight lowering in the transition temperatures.

The melting-like transitions of Na_{142} , Na_{92} , and Na_{55} have been investigated by applying an orbital-free, density-functional molecular dynamics method. The computational effort which is required is modest in comparison with the traditional Car-Parrinello Molecular Dynamics technique based on Kohn-Sham orbitals, that would be very costly for clusters of this size. Specifically, the computational effort to update the electronic system scales linearly with the system size N , in contrast to the N^3 scaling of orbital-based methods. This saving allows the study of large clusters. However, the price to pay is an approximate electron kinetic energy.

An icosahedral isomer of Na_{142} melts in two steps as evidenced by the thermal indicators. Nevertheless, there are isomerization transitions involving surface defects at a temperature as low as 130 K, that preserve the icosahedral structure and do not give rise to any pronounced feature in the caloric curve. The transition at $T_s \approx 240$ K from that isomerization regime to a phase in which the surface atoms acquire a substantial diffusive motion is best described as surface melting. This is followed at $T_m \approx 270$ K by homogeneous melting. For Na_{92} , there is a minor peak in C_v at $T_s \approx 130$ K which we associate with surface melting. The smaller value of T_s , for this cluster compared with Na_{142} , is due to the less ordered surface. Na_{55} , being a perfect two-shell icosahedron with no surface defects melts in a single stage at 190 K. In all cases, for $T > T_m$ the atoms are able to diffuse throughout the cluster volume. Both the calculated T_m at which homogeneous melting occurs and the estimated latent heat of fusion q_m are in excellent agreement with the experimental results of Haberland and coworkers for Na_{142}

and Na_{92} ; our earlier results on the melting of Na_8 ²⁰ are also consistent with the variation of the measured optical spectrum with temperature. A serious discrepancy between theory and experiment remains for Na_{55} .

We have found that structural quantities obtained from the simulations which are very useful in the study of melting in small clusters,²⁰ such as the diffusion coefficient, are not, in the case of the larger clusters studied here, efficient indicators of homogeneous melting, which is better located with thermal indicators. A better structural indicator is the evolution with temperature of the average radial ion density. This quantity flattens when homogeneous melting occurs.

ACKNOWLEDGEMENTS: We would like to thank H. Haberland, S. Kümmel and F. Calvo for sending us preprints of their respective works prior to publication. This work has been supported by DGES (Grants PB95-0720-C02-01 and PB98-D345), NATO(Grant CRG.961128) and Junta de Castilla y León (VA28/99). A. Aguado acknowledges a graduate fellowship from Junta de Castilla y León. M. J. Stott acknowledges the support of the NSERC of Canada and an Iberdrola visiting professorship at the University of Valladolid.

Captions of Figures.

Figure 1 Caloric and specific heat curves of Na_{142} , taking the internal cluster temperature as the independent variable. The deviation around the mean temperature is smaller than the size of the circles.

Figure 2 Caloric and specific heat curves of Na_{92} , taking the internal cluster temperature as the independent variable. The deviation around the mean temperature is smaller than the size of the circles.

Figure 3 Caloric and specific heat curves of Na_{55} , taking the internal cluster temperature as the independent variable. The deviation around the mean temperature is smaller than the size of the circles.

Figure 4 Short-time averaged distances $\langle r_i(t) \rangle_{sta}$ between each atom and the center of mass in Na_{142} , as functions of time for the icosahedral isomer at $T = 30$ K.

Figure 5 Short-time averaged distances $\langle r_i(t) \rangle_{sta}$ between each atom and the center of mass in Na_{142} , as functions of time for the icosahedral isomer at $T = 160$ K. The bold lines follow the evolution of a particular atom in the surface shell and another in the outermost core shell.

Figure 6 Short-time averaged distances $\langle r_i(t) \rangle_{sta}$ between each atom and the center of mass in Na_{142} , as functions of time at $T = 361$ K. The bold lines are to guide the eye in following the diffusive behavior of specific atoms.

Figure 7 Time averaged radial atomic densities of the icosahedral isomer of Na_{142} , at some representative temperatures.

Figure 8 Diffusion coefficient as a function of temperature for the icosahedral isomer of Na_{142} .

Figure 9 Calculated melting temperatures, compared with the experimental values. The experimental values

for the larger cluster sizes are taken from ref. 6, while that for the smallest Na_8 cluster is taken from ref. 35 (see text for details).

-
- ¹ C. Ellert, M. Schmidt, C. Schmitt, T. Reiners, and H. Haberland, Phys. Rev. Lett. **75**, 1731 (1995); P. Brockhaus, K. Wong, K. Hansen, V. Kasperovich, G. Tikhonov, and V. Kresin, Phys. Rev. A **59**, 495 (1999).
 - ² Z. L. Wang, J. M. Petroski, T. C. Green, and M. A. El-Sayed, J. Phys. Chem. B **102**, 6145 (1998).
 - ³ T. P. Martin, Phys. Rep. **273**, 199 (1996).
 - ⁴ K. F. Peters, J. B. Cohen, and Y. W. Chung, Phys. Rev. B **57**, 13430 (1998).
 - ⁵ M. Maier-Borst, D. B. Cameron, M. Rokni, and J. H. Parks, Phys. Rev. A **59**, R3162 (1999).
 - ⁶ M. Schmidt, R. Kusche, W. Kronmüller, B. von Issendorff, and H. Haberland, Phys. Rev. Lett. **79**, 99 (1997); M. Schmidt, R. Kusche, B. von Issendorff, and H. Haberland, Nature **393**, 238 (1998); R. Kusche, Th. Hippler, M. Schmidt, B. von Issendorff, and H. Haberland, Eur. Phys. J. D **9**, 1 (1999).
 - ⁷ J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986); H. L. Davis, J. Jellinek, and R. S. Berry, *ibid.* **86**, 6456 (1987); T. L. Beck, J. Jellinek, and R. S. Berry, *ibid.* **87**, 545 (1987); J. P. Rose and R. S. Berry, *ibid.* **96**, 517 (1992); *ibid.* **98**, 3246 (1993); *ibid.* **98**, 3262 (1993); V. K. W. Cheng, J. P. Rose, and R. S. Berry, Surf. Rev. Lett. **3**, 347 (1996); F. Calvo and P. Labastie, J. Phys. Chem. B **102**, 2051 (1998); J. P. K. Doye and D. J. Wales, Phys. Rev. B **59**, 2292 (1999); J. Chem. Phys. **111**, 11070 (1999); A. Bulgac and D. Kusnezov, Phys. Rev. Lett. **68**, 1335 (1992); Phys. Rev. B **45**, 1988 (1992); N. Ju and A. Bulgac, Phys. Rev. B **48**, 2721 (1993); M. Fosmire and A. Bulgac, *ibid.* **52**, 17509 (1995); Z. Phys. D **40**, 458 (1997); A. Bulgac, Z. Phys. D **40**, 454 (1997); J. M. Thompson and A. Bulgac, *ibid.* **40**, 462 (1997); C. Rey, L. J. Gallego, J. García-Rodeja, J. A. Alonso, and M. P. Iñiguez, Phys. Rev. B **48**, 8253 (1993); J. García-Rodeja, C. Rey, L. J. Gallego, and J. A. Alonso, *ibid.* **49**, 8496 (1994); L. J. Lewis, P. Jensen, and J. L. Barrat, *ibid.* **56**, 2248 (1997); S. K. Nayak, S. N. Khanna, B. K. Rao, and P. Jena, J. Phys.: Condens. Matter **10**, 10853 (1998).
 - ⁸ C. L. Cleveland, W. D. Luedtke, and U. Landman, Phys. Rev. Lett. **81**, 2036 (1998); Phys. Rev. B **60**, 5065 (1999).
 - ⁹ F. Calvo and F. Spiegelmann, Phys. Rev. Lett. **82**, 2270 (1999); J. Chem. Phys. **112**, 2888 (2000).
 - ¹⁰ R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985); M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
 - ¹¹ U. Röthlisberger and W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).
 - ¹² A. Rytönen, H. Häkkinen, and M. Manninen, Phys. Rev. Lett. **80**, 3940 (1998).
 - ¹³ W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133A (1965).
 - ¹⁴ P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864B (1964).
 - ¹⁵ M. Pearson, E. Smargiassi, and P. A. Madden, J. Phys.: Condens. Matter **5**, 3221 (1993); E. Smargiassi and P. A. Madden, Phys. Rev. B **49**, 5220 (1994); M. Foley, E. Smargiassi, and P. A. Madden, J. Phys.: Condens. Mat-

- ter **6**, 5231 (1994); E. Smargiassi and P. A. Madden, Phys. Rev. B **51**, 117 (1995); *ibid.* **51**, 129 (1995); M. Foley and P. A. Madden, *ibid.* **53**, 10589 (1996); B. J. Jesson, M. Foley, and P. A. Madden, *ibid.* **55**, 4941 (1997); J. A. Anta, B. J. Jesson, and P. A. Madden, *ibid.* **58**, 6124 (1998).
- ¹⁶ N. Govind, Y. A. Wang, and E. A. Carter, J. Chem. Phys. **110**, 7677 (1999).
- ¹⁷ V. Shah, D. Nehete, and D. G. Kanhere, J. Phys.: Condens. Matter **6**, 10773 (1994); D. Nehete, V. Shah, and D. G. Kanhere, Phys. Rev. B **53**, 2126 (1996); V. Shah and D. G. Kanhere, J. Phys.: Condens. Matter **8**, L253 (1996); V. Shah, D. G. Kanhere, C. Majumber, and G. P. Das, *ibid.* **9**, 2165 (1997); A. Vichare and D. G. Kanhere, J. Phys.: Condens. Matter **10**, 3309 (1998); A. Vichare and D. G. Kanhere, Eur. Phys. J. D **4**, 89 (1998); A. Dhavale, V. Shah, and D. G. Kanhere, Phys. Rev. A **57**, 4522 (1998).
- ¹⁸ N. Govind, J. L. Mozos, and H. Guo, Phys. Rev. B **51**, 7101 (1995); Y. A. Wang, N. Govind, and E. A. Carter, *ibid.* **58**, 13465 (1998).
- ¹⁹ P. Blaise, S. A. Blundell, and C. Guet, Phys. Rev. B **55**, 15856 (1997).
- ²⁰ A. Aguado, J. M. López, J. A. Alonso, and M. J. Stott, J. Chem. Phys. **111**, 6026 (1999).
- ²¹ *Theory of the inhomogeneous electron gas*. Editors S. Lundqvist and N. H. March. Plenum Press, New York (1983).
- ²² W. Yang, Phys. Rev. A **34**, 4575 (1986).
- ²³ J. P. Perdew, Phys. Lett. A **165**, 79 (1992).
- ²⁴ J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ²⁵ D. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- ²⁶ C. Fiolhais, J. P. Perdew, S. Q. Armster, J. M. McLaren, and H. Brajczewska, Phys. Rev. B **51**, 14001 (1995); *ibid.* **53**, 13193 (1996).
- ²⁷ F. Nogueira, C. Fiolhais, J. He, J. P. Perdew, and A. Rubio, J. Phys.: Condens. Matter **8**, 287 (1996).
- ²⁸ L. Verlet, Phys. Rev. **159**, 98 (1967); W. C. Swope and H. C. Andersen, J. Chem. Phys. **76**, 637 (1982).
- ²⁹ J. M. Montejano-Carrizales, M. P. Iñiguez, J. A. Alonso, and M. J. López, Phys. Rev. B **54**, 5961 (1996).
- ³⁰ S. Sugano, *Microcluster Physics*, Springer-Verlag, Berlin (1991).
- ³¹ S. Kümmel, P. -G. Reinhard, and M. Brack, Eur. Phys. J. D **9**, 149 (1999); S. Kümmel, M. Brack, and P. -G. Reinhard, unpublished results.
- ³² B. Montag and P. -G. Reinhard, Z. Phys. D **33**, 265 (1995).
- ³³ T. P. Martin, T. Bergmann, H. Göhlich, and T. Lange, Z. Phys. D **19**, 25 (1991).
- ³⁴ Z. B. Güvenc and J. Jellinek, Z. Phys. D **26**, 304 (1993).
- ³⁵ M. Schmidt, C. Ellert, W. Kronmüller, and H. Haberland, Phys. Rev. B **59**, 10970 (1999).
- ³⁶ H. Haberland, in “*Metal Clusters*”, ed. W. Ekardt (John Wiley & Sons, 1999), p. 181.
- ³⁷ V. Bonacić-Koutecký, J. Jellinek, M. Wiechert, and P. Fantucci, J. Chem. Phys. **107**, 6321 (1997); D. Reichardt, V. Bonacić-Koutecký, P. Fantucci, and J. Jellinek, Chem. Phys. Lett. **279**, 129 (1997).

















